Supra–Supra, Supra–Antara, and Stepwise-Diradical Pathways for an Observed 16-Electron Double-[4 + 4] Cycloaddition within Metal-Templated Dialkyne Dimers $(PtX_2)_2(\mu-R_2PCCCCPR_2)_2$

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ABSTRACT: Quantum chemistry calculations are used to provide insight into the cycloaddition of two dialkyne chains in initially monocyclic organoplatinum dimers of the type $(PtX_2)_2(\mu$ -R₂PC₄PR₂)_2, where X = Cl or Me and R = Ph or Me. Previous experimental studies showed that the cycloaddition occurs with $\{X, R\} = \{Cl, Ph\}$ but not $\{Me, Ph\}$. Two concerted pericyclic paths, a D_{2h} -symmetry double- $[\pi 4s + \pi 4s]$ "Hückel path" and a D_{2r} -symmetry double- $[\pi 4s + \pi 4s]$ "Möbius path", were explored via orbital energy correlation diagrams (OECDs) computed using a singly occupied molecular orbital technique developed earlier. In accord with pericyclic reaction theory, the $16e^-$ rearrangement is forbidden along the D_{2h} Hückel path; four electrons would need to change their orbital symmetries.



The D_2 Möbius path, afforded by the natural twist in the reactant structure which allows the desired Möbius orbital connectivity for a 4n rearrangement, is concluded to be a borderline forbidden pathway. This Möbius path creates avoided crossings in the OECD, which allows consistent orbital populations throughout the reaction, but it does not cause a change in intended orbital correlation, and the predicted activation barrier is rather high (~50 kcal mol⁻¹). The avoided crossings show strong coupling, but a clear HOMO–LUMO gap for the reaction is not produced. A stepwise path is also presented, with evidence of its diradical character.

INTRODUCTION

In pericyclic reaction theory, rules for predicting whether such additions are allowed or forbidden were put forward many years ago by Woodward and Hoffmann based on conservation of orbital symmetry,¹ and these rules have been based on other concepts such as transition-state aromaticity² and basis-orbital phase alternations.³ The rules are not quantitative, as they do not address how allowed or how forbidden a reaction should be, and quantitative metrics would be useful for assessing or predicting borderline cases. As a motivating example, the set of Diels—Alder reactions studied by Spino, Rezaei, and Dory showed varying degrees of reactivity and a breakdown in the expected correlation with initial HOMO—LUMO energy gap.⁴ An example of theoretical interest in this topic is Sakai's exploration of several reactions with a computational measure of the degree of aromaticity of transition states.⁵

Pericyclic reaction theory is expected to apply to *metal-templated* cycloadditions, but not metal-catalyzed ones. By metal-templated we mean organometallic reactions in which the template metal atoms do not serve as the reaction center, but rather as the "hands" that hold the substrates in close proximity.⁶ Metal-templated cycloadditions offer some potential benefits over traditional (and well-established⁷) transition-metal-catalyzed cycloadditions, particularly in improved control of regioselectivity and enantioselectivity.^{8,9} Both metal-templated and metal-catalyzed cycloadditions by turning bi- or termolecular reactions into monomolecular ones. Some dramatic examples in metal-catalyzed alkyne cycloaddition include the "[2+2+2]" (or possibly, double-[2+2+2]) synthesis of benzene rings,¹⁰

and the $16e^{-}$ "[2+2+2+2]" (properly, double-[2+2+2+2]) synthesis of cyclooctatetraene rings.^{11,12}

We are interested in metal-templated intramolecular coupling reactions of phosphinoalkynes.^{13–17} Specifically, the current paper addresses the apparent 16e⁻ double-[4+4] cycloaddition of two divne substrates to form a cyclooctadienedivne ring, $1 \rightarrow 2$ (Figure 1), described by Martin-Redondo et al.¹⁵ In this reaction, cycloaddition of two bisdiphenylphosphinobutadiyne substrates is templated by coordination of the substrate to PtCl₂ metal templates. We seek to understand two mysteries. The first is why the $1a \rightarrow 2a$ reaction is rapid at only 40 °C in CH₂Cl₂ solvent, and even occurs below 0 °C and in the solid state,¹⁵ despite the pericyclic theory prediction that the straightforward suprafacial-suprafacial double- $[\pi 4s + \pi 4s]$ approach of the divines is anti-Hückel (4*n* electrons rather than 4n+2) and therefore forbidden. The second is why the templated cycloaddition reaction is sensitive to the ligands on Pt, since the $1b \rightarrow 2b$ reaction does not occur under mild conditions.¹⁵ These questions led us to not only apply pericyclic reaction theory but to seek quantitative metrics for it.

The X-ray crystal structure of **1b** (Figure 2) shows the two alkyne strands in a crossed, D_2 -symmetry structure, caused by the square-planar geometry about platinum and the tetrahedral geometry about phosphorus. One assumes that **1a**, which could not be isolated, has a similar structure. This crossed starting structure led us to hypothesize, for the first mystery, that the

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Figure 1. Cycloaddition reaction of interest. The hypothetical reactions $1c_{,d} \rightarrow 2c_{,d}$ were used as computational models of the experimentally¹⁵ attempted $1a_{,b} \rightarrow 2a_{,b}$.



Figure 2. X-ray crystal structure of 1b from an earlier study.⁹ Phenyl carbons, except for ipso carbons, have been omitted for clarity.



Figure 3. $C_{24}H_{32}$ hydrocarbon model reaction used for OECD generation.

reaction could be considered a supra—antara double- $[\pi 4s + \pi 4a]$ approach and thus capable of Möbius orbital connectivity³ and therefore "allowed." For the second mystery it has been hypothesized¹⁶ that the reactivity difference of **1a** vs **1b** is due to the proximity of the two diyne strands in the two structures, in line with an earlier hypothesis for trimers.¹⁵ The goal of this study was to test these two hypotheses.

The hypothesis for the second mystery will be tested with traditional geometry-optimization calculations, but the Möbius hypothesis for the first mystery requires nonstandard effort. For this, orbital-energy correlation diagrams (OECDs) will be generated, for both D_{2h} (supra-supra, Hückel-like) and D_2 (supra-antara, Möbius-like) reaction paths. In an OECD, a reaction is said to be forbidden if there are occupied orbitals in the reactant that correlate with unoccupied orbitals in the product, and vice versa, such that their orbital energies are seen to cross. According to Woodward and Hoffmann, if there is loss of symmetry that forces these crossings to be avoided crossings, the reaction should be considered "no less forbidden."¹ Penciland-paper OECDs for reactions involving a large number of electrons rearranging, and particularly for alkyne additions, would be highly approximate due to the high density of orbital energies which causes energy perturbations via mixing. Fortunately, OECDs can now be generated using a SOMO (singly occupied molecular orbital) OECD technique, named here but developed earlier by one of us,¹⁸ and described below in the

Methods section. This technique requires a hydrocarbon model for the reaction system; in the current study the $C_{24}H_{32}$ model reaction is $3 \rightarrow 4$, shown in Figure 3.

THEORETICAL METHODS

All calculations were performed using the Gaussian03 software package.¹⁹ Geometry optimizations were performed with the PW91 level of density functional theory (PW91PW91 keyword);²⁰ these include attempts at thermally allowed (ground-state) transition-state optimizations where we have used the opt=(ts,noeigentest,calcfc) algorithm. Basis sets are taken from Gaussian03's library,¹⁹ as follows. For platinum-containing complexes $(1 \rightarrow 2)$, the mixed basis set combination LANL2DZ: cc-pVDZ:STO-3G was used: LANL2DZ for Pt atoms, cc-pVDZ for P and the main eight C atoms (in the initial ring of 1), and STO-3G for all atoms in the X and R groups. The LANL2DZ basis set provides, for Pt, functions for the 5s and 5p near-valence orbitals as well as the 6s, 5d, and 6p valence orbitals, and a relativistic effective core potential to represent the other occupied orbitals. For the hydrocarbon model $(3 \rightarrow 4)$, the combination cc-pVDZ:STO-3G was used for the optimizations: cc-pVDZ for the main eight C atoms (as with 1) and STO-3G for all other atoms. This combination was also used with Gaussian's completeactive-space (CAS) SCF algorithm²¹ for a diradical test.

A computational technique for generating an orbital-energy correlation diagram (OECD) would involve computation of orbital energies at several molecular positions along the reaction path. Since the orbital energy definition depends on occupation,²² an orbital whose occupation might "change" along a reaction path would produce a discrete jump in its energy. Our recent strategy,¹⁸ which we now dub the SOMO OECD technique (SOMO = singly occupied molecular orbital), cures this problem by placing only one alpha-spin electron in every valence orbital, regardless of the usual occupancy of the orbital. In our case with the hydrocarbon model $(3 \rightarrow 4)$, we have charge = 0 and multiplicity = 129. One could instead place zero (or two) electrons in every valence orbital to be consistent, but this leads to a buildup of charge on the molecule, which can lead to unphysical rises or dips in the entire OECD.¹⁸ Choosing a hydrocarbon for the SOMO calculations is desirable because then the all-SOMO system has zero net charge (e.g., each C atom contributes four electrons and four valence orbitals). SOMO energies were computed with restricted open-shell Hartree-Fock (ROHF keyword) and the STO-3G minimal basis set, as this was sufficient in the earlier N_2 + O_2 project.¹⁸ Calculations with the cc-pVDZ basis set for all atoms were also tried but were plagued by state convergence problems at certain midpath locations.

RESULTS

Stationary Points and Orbital Occupations. The geometries of structures 1a-d (D_2 symmetry) and 2a-d (D_{2h} symmetry) were optimized, and selected results appear in Table 1. We immediately have support for the earlier hypothesis¹⁶ for the second mystery, i.e., that the enhanced reactivity of 1a (Pt₂Cl₄P₂Ph₈C₈) vs 1b (Pt₂Me₄P₂Ph₈C₈) is due to the "alpha– alpha" $R(C_1C_8)$ distance being closer in 1a versus 1b. Athough there is an absolute error of +0.1156 Å in the predicted $R(C_1C_8)$ value of 1b, what is important is the more-accurately predicted relative shift of -0.11 Å when replacing the methyl groups (1b)

Table 1. Reactant a	nd Product D	0ata from PW9	1 Optimizations,	, Pt-Containing	Models
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molecule	$R(C_1C_8)$ (Å)	R(PtP) (Å)	$\theta(\text{PPtP})$ (°)	$\Phi(C_8C_1C_4C_5)~(^\circ)$	$\Phi(C_2C_1C_8C_7)(^\circ)$	ΔE , kcal mol $^{-1}$	
1a	3.3250	2.2660	110	34	-30	_	
$1b^a$	3.4371	2.3428	104	37	-34	_	
1c	3.3570	2.2663	111	22	-18	_	
1d	3.4622	2.3433	104	36	-32	_	
2a	1.3854	2.2318	91	3.0	-4	-33	
2b	1.3848	2.3219	87	3.5	-5	-31	
2c	1.3887	2.2265	90	0	0	-27	
2d	1.3839	2.3180	86	0	0	-28	
¹ Experimental values (ref 16) for compound 1b in the crystalline state: $R(C_1C_8) = 3.3215$ Å, $R(PtP) = 2.278$ Å, $\Phi(C_2C_1C_8C_7) = 34^\circ$.							

with chloro groups (1a). Such a shift, when applied to the experimental value for 1b (3.3215 Å), then predicts a value of 3.21 Å for 1a, matching the 3.2 Å criterion for reactivity estimated in that earlier study. This shrinkage likely lowers the activation barrier by raising the relative starting energy in 1a vs 1b, due to extra strain in the P–Pt–P angle (110° vs 104°) caused by the shorter Pt–P bond lengths (2.27 vs 2.34 Å).

For the hydrocarbon model needed for the OECDs, the replacement of $PR_2-PtX_2-PR_2$ with four methylene groups resulted in an enantiomeric pair of D_2 -symmetry structures for the product (4) and four D_2 structures (2 conformers times 2 enantiomers each) of the reactant (3). Both conformers of 3 (initially separated in energy by 12 kcal mol⁻¹) lead to the one and only conformer of 4, and both do so via a stationary point with 3 imaginary frequencies, as in the $1c \rightarrow 2c$ case. The lower-energy conformer of 3 and its path to 4 were chosen for this study.

Also required for the OECDs were an optimized geometry somewhere along each $3 \rightarrow 4$ path. For D_{2h} an intermediate 5 was found, of an electronic state different from both the reactant and the product. For D_2 a "transition state" was optimized, having the same electronic state (same orbital occupancy) as reactant and product; its three imaginary frequencies do not preclude it from use in Möbius path generation, although this was a clue to a different discovery (see the last section of the Article).

Figure 4 presents images of several of these optimized geometries.

Table 2 presents selected data, including orbital occupations, from these stationary point optimizations. For the first path (D_{2h}) $1c' \rightarrow 2c$), the orbital occupations of 1c' and 2c are not identical, and this is sufficient to explain why supra-supra attack cannot be thermally allowed. For the second path $(D_2 \ \mathbf{1c} \rightarrow \mathbf{2c})$, the orbital occupations of 1c and 2c are identical, but the question remains whether this supra-antara path is "allowed" due to good orbital correlations or if it is merely benefitting from avoided crossings of orbital energies and thus should still be considered "forbidden." Hence, within D_2 symmetry, an OECD is desired to probe the issue further, requiring the hydrocarbon model reaction $3 \rightarrow 4$. Note from the third and fourth rows of Table 2 that this $C_{24}H_{32}$ model also exhibits the orbital occupation trends of the PtCl₂ model, i.e., consistent along the D_2 path and inconsistent along the D_{2h} path. It also shows reasonable agreement in reaction exothermicity from minimum to minimum $(-35 \text{ kcal mol}^{-1} \text{ for } 3 \rightarrow 4, \text{ versus } -27 \text{ for } -27 \text{ for$ $1c \rightarrow 2c$). (The large number of imaginary frequencies for the D_{2h} path of the hydrocarbon $(3' \rightarrow 4)$ is due to the strain of the end rings, whose carbon nuclei are forced to be planar.)

This comparison of $3 \rightarrow 4$ to $1c \rightarrow 2c$ indicates that the $C_{24}H_{32}$ model is an acceptable mimic for the Pt-containing molecules in terms of the electronic nature of the reaction, and

hence OECDs arising from calculations of $3 \rightarrow 4$ are fully applicable to $1 \rightarrow 2$.

Construction of the Supra-Antara OECD. To correlate orbitals by symmetry, a computed OECD requires a common point group at all geometries chosen; for supra-antara attack we employed D_2 symmetry. The model hydrocarbon reaction from reactant to product $(3 \rightarrow 4)$ was used.

To choose points along a reaction path within D_2 symmetry, various techniques can be used. Intrinsic reaction coordinates or other minimum-energy paths can be used but only for thermally allowed reactions. Instead, to be more general, we first tried parabolic fitting through the optimized "transition state" in D_2 symmetry, by choosing an internal coordinate set and fitting each internal coordinate λ_i through its values at the three previously optimized points (reactant, transition state, product) with a parabolic function: $\lambda_i(t) = a_i t^2 + b_i t + c_i$, where t ("time") values were chosen to be -4 for reactant, 0 for TS, and +4 for product. However, this failed to give a realistic path due to overstretching of certain C–C bond distances at $t = \pm 2$, likely due to the multiply ringed nature of the molecule and the inability to include all bond distances in the internal coordinate set.

Therefore, we settled on a minimum-energy path technique, since the consistent orbital occupations for $3 \rightarrow TS \rightarrow 4$ (Table 2) hinted that the reaction might be thermally allowed. This technique selects one crucial internal coordinate, holds it fixed at various values between its initial and final value, and optimizes all other coordinates to minimize the ground-state energy at each choice. In the current study, $R(C_1C_8)$ was the coordinate fixed, at values between 4.11 (reactant) and 1.38 Å (product). An internal-coordinate *Z*-matrix involving five dummy atoms was chosen to maintain D_2 symmetry, and scf=(qc, intrep) was needed to obtain SCF convergence.

Initial plotting of the OECD as a function of $R(C_1C_8)$ resulted in a skewed plot with large gradients in a small region. A smoother plot was obtained by defining the reaction coordinate to be 90% of $R(C_1C_8)$ and 10% of the twist dihedral Φ - $(C_1C_8C_5C_4)$; the coordinate definition was $X_n = 9(R_n - R_i)/(R_f - R_i) + (\Phi_n - \Phi_i)/(\Phi_f - \Phi_i)$, where the subscript *n* is an index denoting a particular restricted optimization. X_n takes on values between 0(reactant) and 10(product), and calculated values appear in Table 3.

Orbital energies, using the SOMO technique, were computed at these 14 points along the D_2 path. To use these to make an OECD, we require that the axis convention for the b_1 , b_2 , and b_3 symmetry labels of D_2 be consistent with the long (L), short (S), and perpendicular (P) axes of the molecule everywhere along the path. However, the Gaussian program chooses axes conventions based on the rotational constant magnitudes, which causes an



Figure 4. Images of PW91-optimized structures for $1c \rightarrow 2c$, viewed down the "perpendicular" axis (left images) and down the "short" axis (right images). Pt/Cl/P/C/H atoms are blue/green/orange/gray/white, respectively.

axis identity swap twice along this path (footnote to Table 3). The inconsistency was cured by using these SPL symmetry labels instead: by replacing molecular orbital symmetry labels $\{a, b_1, b_2, b_3\}$ from Gaussian with $\{A, S, P, L\}$ in the swapped region and with $\{A, P, S, L\}$ at either end.

The OECDs. Figure 5 is the resulting supra-antara (D_2) OECD, generated from $3 \rightarrow 4$, displaying the energies of 24 orbitals plotted versus X_n . The lowest 12 of these 24 would be occupied in the reaction. For comparison, Figure 6 presents the supra-supra (D_{2h}) OECD, generated from SOMO data calculated only at the three D_{2h} stationary points of Table 2 $(3' \rightarrow 5 \rightarrow 4')$. No additional restricted optimizations were performed

for Figure 6 because of the inability to maintain a common state along the entire path. In Figure 6 the energies of 20 orbitals are plotted, of which the lowest 10 would be occupied.

The orbital occupation analysis of the optimized D_{2h} structures (Table 2) already ruled out the possibility of a thermally allowed supra—supra path. Indeed, in the supra—supra OECD (Figure 6), the reactant HOMO and HOMO–1 (labeled P_{σ} and A_{π}) rise in energy and cross with two others (P_{π} and A_{σ}) that are normally occupied in the product. Orbital symmetry is not conserved, and therefore the reaction path is thermally forbidden. This matches the prediction by the usual electron counting rule for suprafacial attack (4n =forbidden).

Tab	le 2.	Symmetric-Path	Stationary-Poin	t Data from PW91	Optimizations
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path	structure	$E_{\rm relative}~({\rm kcal}~{\rm mol}^{-1})$	orbital occupation ^{<i>a,b</i>}	imaginary frequencies (cm^{-1})
D_{2h} path, $1c' \rightarrow 2c$	$1c'(D_{2h})$	0 ^{<i>c</i>}	27, 26; 10,10; 11,11; 23, 24	none
	2c (D_{2h})	-27	28, 26; 10, 9; 11, 12; 22, 24	none
D_2 path, $1c \rightarrow 2c$	1c (D_2)	0	37; 36; 35; 34	none
	2c (D_{2h})	-27	37; 36; 35; 34	none
D_{2h} path, $\mathbf{3'} \rightarrow 4$	$3'(D_{2h})$	+75	16, 7; 15, 7; 15, 7; 14, 7	303 <i>i</i> , 303 <i>i</i> , 92 <i>i</i> , 91 <i>i</i> , 52 <i>i</i> , 27 <i>i</i>
	5 (D_{2h})	+15	17, 7; 15, 7; 15, 7; 13, 7	218 <i>i</i> , 218 <i>i</i> , 101 <i>i</i> , 64 <i>i</i> , 58 <i>i</i>
	$4'(D_{2h})$	-14	17, 6; 15, 7; 15, 7; 13, 8	204 <i>i</i> , 204 <i>i</i> , 45 <i>i</i> , 42 <i>i</i>
D_2 path, $3 \rightarrow 4$	$3(D_2)$	0	23; 22; 22; 21	none
	TS (D_2)	52	23; 22; 22; 21	449 <i>i</i> , 344 <i>i</i> , 140 <i>i</i>
	$4(D_2)$	-35	23; 22; 22; 21	none

^{*a*} D_2 symmetry convention: all; long; short; perpendicular, with the terms denoting the C^2 axes about which the orbital is symmetric (produces +1 character). ^{*b*} D_{2h} symmetry convention: $a_{gr} b_{3gr} a_{ui} b_{2gr} b_{1gr} b_{2ur}$ where the commas couple irreps that correlate to the same irrep in $C_{2\nu}$ symmetry, e.g., a_g and b_{3u} both become a_1 in $C_{2\nu}$ symmetry. ^{*c*} This untwisted conformer of 1c is lower than 1c by 0.1 kcal mol⁻¹.

Table 3. Reaction Coordinate Values X_n , Rotational Con-
stants $\{A_n, B_n, C_n\}$, and Ground-State Energy, for D_2 Mini-
mum-Energy Path of C ₂₄ H ₃₂ at Locations of Restricted
Optimization

	R_n	Φ_n		A_n	B_n	C_n	energy
п	(Å)	(°)	X_n	(GHz)	(GHz)	(GHz)	(au)
8(reac)	4.11	28.9	0.000	0.287	0.138	0.115	-927.6248
7	3.45	39.4	1.764	0.311	0.136	0.122	-927.6180
6	2.88	50.3	3.206	0.335	0.137	0.135	-927.5962
5	2.40	56.8	4.526	0.360	0.149 ^a	0.142 ^{<i>a</i>}	-927.5626
4(TS)	2.01	59.8	5.689	0.376	0.155 ^a	0.146 ^a	-927.5421
3.75	1.93	59.4	5.967	0.379	0.154 ^{<i>a</i>}	0.147 ^a	-927.5437
3.5	1.85	57.6	6.294	0.381	0.150 ^a	0.147 ^a	-927.5488
3.25	1.78	50.9	6.796	0.382	0.146	0.139	-927.5594
3	1.72	33.8	7.696	0.383	0.148	0.125	-927.5790
2.75	1.66	13.2	8.719	0.387	0.150	0.120	-927.6035
2.25	1.56	7.59	9.281	0.394	0.151	0.122	-927.6437
2	1.51	6.29	9.473	0.397	0.152	0.122	-927.6577
1	1.40	4.22	9.924	0.406	0.153	0.124	-927.6796
0(prod)	1.38	3.97	10.000	0.407	0.154	0.124	-927.6803
⁴ For these points, the identities of the $\{B, C\}$ principal axes were $\{P, S\}$;							
otherwise,	they a	are {3, 1	۳ ;.				

In the supra-antara OECD (Figure 5), however, the two red orbitals P_{π} and P_{σ} have the same symmetry (P) due to the reduction of symmetry from D_{2h} to D_2 , and although they have very little overlap with each other when at the pseudo- D_{2h} geometries of the reactant and product, they overlap (couple) substantially in the mid-to-late moments of the reaction, resulting in an avoided crossing. In this case, a substantial orbital energy gap of 0.07 au is maintained between these two P-symmetry orbitals, throughout the reaction. A similar situation occurs with the A_{π} and A_{σ} orbitals. An avoided crossing causes a continual transmutation or "morphing" of one orbital into the other during the course of reaction, as demonstrated in Figure 7. Note especially the vivid demonstration of Möbius orbital connectivity, manifested in interweaved density lobes at the intermediate geometry (middle column).

Should this supra-antara double- $[\pi 4s + \pi 4a]$ pericyclic reaction mechanism be considered allowed or forbidden? Switching from a D_{2h} path to a D_2 one *did not alter* the intended orbital



Figure 5. ROHF/STO-3G SOMO OECD for double- $[\pi 4s + \pi 4a]$ (D_2 -symmetry) attack. P σ is the normal HOMO of the reactant diyne dimer (left side of figure).



Figure 6. ROHF/STO-3G SOMO OECD for double- $[\pi 4s + \pi 4s]$ (D_{2h} -symmetry) attack. P σ is the normal HOMO of the reactant divine dimer (left side of figure).

correlations; from Figure 7 it is clear that the 34th P orbital of the reactant looks more like the 35th (rather than the 34th) P orbital of the product, and the 37th A orbital of the reactant looks more like the 38th (rather than the 37th) A orbital of the product. The switching to a Möbius supra-antara path merely created an



Figure 7. Four ROHF/STO-3G orbitals of $C_{24}H_{36}$, showing their evolution along the antarafacial (D_2) reaction path (left to right: $X_n = 3.2$, 6.8, 10 in Table 3). First two rows: the P_{α} and P_{α} orbitals which transmute into each other due to the avoided crossing. Last two rows: the A_{α} and A_{α} orbitals, which similarly transmute into each other.



Figure 8. Zipper-path intermediates, from single-configuration PW91 calculations.

avoided crossing, due to loss of symmetry from D_{2h} to D_2 . Hence this should probably be called "forbidden" by the Woodward/ Hoffmann rules.¹ What makes this case a borderline one is the substantial sizes of the P_{π}/P_{σ} and A_{π}/A_{σ} couplings. These couplings suppress any rise in energy of the occupied 37th A orbital and hold the rise in energy of the occupied 34th P orbital to 0.075 au (47 kcal mol^{-1}). Note the near match of the energy rise of this P orbital to the PW91-computed activation

Table 4.	Zipper-Path	Stationary-Point	Data from	PW91 O	ptimizations
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path	structure	$E_{\rm relative}~({\rm kcal}~{\rm mol}^{-1})$	orbital occupation ^{<i>a,b,c</i>}	imaginary frequencies (cm^{-1})
$1c' \rightarrow 2c$	$\mathbf{1c}' \ (D_{2h})^d$	0	27, 26; 10, 10; 11, 11; 23, 24	none
	$TS_1(C_{2\nu})$	21	53; 20; 22; 47	370 <i>i</i>
	$7(C_{2\nu})$	15	53; 20; 22; 47	none
	$TS_2(C_1)$	38	142	427 <i>i</i>
	$2c(D_{2h})$	-27	28, 26; 9, 10; 11, 11; 22, 24	none
$3 \rightarrow 4$	$3(D_2)$	0	23; 22; 22; 21	none
	$TS_1(C_2)$	27	45; 43	331 <i>i</i>
	6 (C ₂)	24	45; 43	none
	$TS_2(C_1)$	43	88	411 <i>i</i>
	$4(D_2)$	-35	23; 22; 22; 21	none

^{*a*} D_2 symmetry convention: all; long; short; perpendicular, with the terms denoting the C^2 axes about which the orbital is symmetric (produces +1 character). ^{*b*} C_2 symmetry convention: a; b. ^{*c*} $C_{2\nu}$ symmetry convention: a₁; a₂; b₁; b₂. ^{*d*} D_{2h} symmetry convention: a_g, b_{3u}; b_{3g}, a_u; b_{2g}, b_{1u}; b_{1g}, b_{2w} where the commas couple irreducible representations that correlate to the same irreducible representations in $C_{2\nu}$ symmetry, e.g., a_g and b_{3u} both become a₁ in $C_{2\nu}$ symmetry.

energy for this reaction path (52 kcal mol^{-1} , fourth row of Table 2).

The strong couplings are not strong enough to create a consistent HOMO–LUMO gap for the supra–antara reaction, however, as these two orbital energies meet in the second half of the reaction. This aspect, and the large rise and fall of the HOMO energy (which causes the large activation energy for this pathway), leads us to conclude that one should consider this a forbidden but borderline pathway. It would appear that dialkyne strands are too linear to be able to provide a true supra–antara Möbius-strip change in orbital correlations in order to make this reaction allowed. Since the reaction is thermally facile, at least for the case $1a \rightarrow 2a$, and especially since the HOMO and LUMO energies meet, there is a significant possibility that the true reaction might break symmetry to be stepwise and perhaps diradical in character, and this was next explored.

A Stepwise-Diradical "Zipper" Pathway. The hydrocarbon model produced a "transition state" along the D_2 -symmetry Möbius path that had three imaginary frequencies (reported in Table 2): one along the reaction path and two for distortions away from D_2 symmetry. These distortions were pursued with the same level of theory (PW91), and a two-step "zipper" path was discovered, with two transition states and an intermediate. A similar path was found, with some effort, for the PtCl₂ model compound $\mathbf{1c'} \rightarrow \mathbf{2c}$ (but not $\mathbf{1d} \rightarrow \mathbf{2d}$, due to convergence failures). Images of these intermediates appear in Figure 8, and selected data appear in Table 4. The two-step paths offer a ~20% reduction in overall barrier height from the symmetric D_2 Möbius pathways.

This is evidence of diradical behavior, which we proved with a CASSCF(2,2) single-point calculation at the geometry of hydrocarbon intermediate **6**. The CASSCF(2,2) wave function was

$$\Psi_{\rm CAS} = 0.8369 \Psi_0 - 0.5473 \Psi_1$$

where Ψ_1 features a doubly occupied LUMO instead of the doubly occupied HOMO. However, the HOMO and LUMO at this geometry (shown in Figure 9) consist of plus-and-minus mixtures of nearly identical "monomer" orbitals (say, A and B) of each carbon strand. Because of this, Ψ_{CAS} can be rewritten²³ as

$$\Psi_{\text{CAS}} = 0.979 \Psi_{\text{VB}} + 0.205 \Psi_{\text{ionic}}$$

where Ψ_{VB} (the valence-bond wave function) features one odd electron on each strand (A(1)B(2) + B(1)A(2)) and Ψ_{ionic} (the



Figure 9. LUMO (top) and HOMO (bottom) of the intermediate 6, from a single-configuration PW91 calculation.

anion/cation wave function) has these two electrons on one strand (A(1)A(2) + B(1)B(2)). The conversions are $c_{\rm VB} = (c_1 - c_2)/2^{1/2}$ and $c_{\rm ionic} = (c_1 + c_2)/2^{1/2}$ if the overlap between monomer orbitals is assumed zero. Hence the wave function is 95.8% $\Psi_{\rm VB}$ in nature ($0.979^2 \times 100\%$) at this intermediate geometry. Although the valence bond wave function contains both covalent and diradical natures, the distance between strands precludes much covalent interaction, and thus the bulk of this 96% weighting is almost surely due to diradicaloid behavior. Indeed, Davidson and Clark suggested that if the two coefficients in the CASSCF(2,2) expansion are both greater than 0.5 in magnitude, the state is qualitatively diradical.²⁴ To satisfy a referee, a CASSCF(6,6) was also performed, resulting in $\Psi_{\rm CAS} = 0.8111\Psi_0 - 0.5048\Psi_1$ and no other CI coefficient above 0.16.

Density-functional theories like PW91 are able to introduce some nondynamical (multiconfiguration) character,²⁵ which here allowed a single-configuration path to head toward a biradical intermediate, but a proper multiconfiguration treatment would likely reduce the reaction barrier further. Unfortunately, we quickly ran into convergence problems with CASSCF(2,2) at other geometries.

Since there is little diradical character at the reactant or product geometry, the DFT path in Table 4 shows that the reaction can seamlessly gain diradical character adiabatically, i.e., without requiring photochemistry to a second electronic state. This is likely why the reaction proceeds rather easily, at least for $\mathbf{1a} \rightarrow \mathbf{2a}$. Said another way, a *state* correlation plot along this zipper-path coordinate would reveal two avoided crossings between $E(\Psi_0)$ and $E(\Psi_1)$: the first one mixes Ψ_0 and Ψ_1 to form a biradical state and an ion-resonance state at the intermediate geometry, and the second one decouples Ψ_0 and Ψ_1 again on the way to cyclic product. These avoided crossings help to reduce the reaction barrier to be thermally accessible.

CONCLUSIONS

On the issue of the reactivity differences of the $PtCl_2$ (1a) vs $PtMe_2$ (1b) template reactions, the calculations confirm the earlier hypothesis¹⁶ that 1a is reactive because the two dialkyne strands are held more closely together in 1a than in 1b; the speculated 3.2 Å threshold seems correct.

On the issue of the facility of this 16e⁻ rearrangement reaction, orbital energy correlation diagrams (OECDs) for both a D_{2h} -symmetry double- $[\pi 4s + \pi 4s]$ "Hückel path" and a D_{2} symmetry double- $[\pi 4s + \pi 4a]$ "Möbius path" were computed. In accord with pericyclic reaction theory, the supra-supra rearrangement is forbidden; four electrons would need to change their orbital symmetries. The Möbius-style supra-antara rearrangement, suggested by the twist in the reactant structure, is also formally "forbidden" due to the inability of this arrangement to qualitatively change the intended orbital correlations; the avoided crossing created by this path is due largely to the loss of D_{2h} symmetry and hardly benefits from Möbius overlap of the orbitals. The two avoided crossings in the OECD show substantial couplings (0.07 au splitting) but a clear HOMO-LUMO gap for the reaction is not produced, and the predicted activation barrier is rather high (\sim 50 kcal mol⁻¹). Instead, a stepwise zipper pathway via an adiabatically accessible diradical intermediate appears to be the true mechanism for this reaction.

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